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Effects of different processing techniques on multi-walled carbon nanotubes/silicone rubber nanocomposite on tensile strength properties

N Mazlan[1*], M Jaafar[2], A Aziz[2], H Ismail[2] and J J C Busfield[3]

[1]Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia, Malaysia
[2]School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Malaysia
[3]Department of Materials, Queen Mary, University of London, United Kingdom

*norkhairunnisa@upm.edu.my

Abstract. In this work, two different processing techniques were approached to identify the properties of the multi-walled carbon nanotubes (MWCNT) reinforced polydimethylsiloxane (PDMS). The MWCNT was dispersed in the polymer by using the ultrasonic and twin screw extruder mixer. The final composite showed different manner of dispersed tubes in the silicone rubber matrix. High shear twin screw extruder tends to fragment the tubes during processing compound, which can be observed by scanning electron microscope (SEM). Tensile strength of the extrusion MWCNT/PDMS nanocomposites was found to be higher compared to ultrasonic MWCNT/PDMS nanocomposites.

1. Introduction

One dimensional (1D) tubular structure of carbon nanotubes (CNT) has stimulated intensive research due to their unique structure and also improved mechanical, thermal and electronic properties when combined with polymers. The remarkable properties of the CNT are well known and their exploitation for a wide range of applications can replace existing materials. Silicone rubber is a versatile material that makes it flexible above its glass transition temperature (approximately -127^0C). In aerospace applications, polydimethylsiloxane (PDMS) has been used for adhesion for silica thermal protection tile, heat sinks on printed circuit board and also strain isolation pad for space shuttle. In addition, the elasticity of the silicone rubber can be changed by varying its molecular structure, network density, molecular size and functional contents. This further creates various forms of silicone rubber for wider applications.

Recently, great interests have been focused on the development of method for the preparation of CNT composites in exploiting their remarkable properties. The effective utilization of CNT in polymer depends on the homogeneity of the tubes in the matrix resin and on the interfacial adhesion between the tubes wall and the polymer matrix [1, 2]. Unfortunately, it is difficult to disperse CNT in polymeric materials due to nano size of the tubes, close together with high surface energy that induces intrinsic van der Waals interactions between individual tubes that makes the tubes entangled together [2]. Many attempts have been done on dispersing the CNT uniformly in the matrix such as modifying the CNT

surfaces by oxidizing it with mixture of acids or attachment with free radicals on the tube surfaces, physically mix with ultrasound or use high shear mixing instrument and mixture with surfactant or solvents, etc.

Most of the researchers compound the CNT in rubber with aid of solvent by means of ultrasonic to disperse the CNT in the suspension [3, 4]. Besides ultrasonic, others have managed to compound the CNT in rubber by using high shear mixer [5]. It is important to ensure that the processing technique should be less damaging to the integrity of the tube surfaces. If the CNT was badly digested during dispersions, the conductivities of the CNT composites could be poor [6]. Inadequate dispersion not only reduces the filler-matrix interaction but also shows different concentrations of matrix and CNT boundaries in the composites, which reduce the desirable properties of the CNT composite. A common method for preparing CNT polymer composite is simply by mixing the CNT with solvent or aqueous solutions of the polymer and evaporating the solvents in a controlled way. Ultrasonic can be used to disperse the CNT in various solvent or liquid polymer [7]. The low viscosity of the solution allows the tubes to move freely through the matrix during the sonicated process. Hernandez *et al.* [8] used both types of ultrasonic, which are ultrasonic bath and ultrasonic tips, to prepare stock dispersion of CNT in polyvinyl alcohol (PVA)-water solution. The drawback of the sonication process is not only limited to polymers, which are freely dissolved in common solvents, but also take a long time to break down the aggregate materials as to uniformly disperse through the liquid medium [9, 10]. Lack of processing time reduces the efficiency to break down the aggregate CNT into individual tubes and less uniformity of the tubes dispersion [11]. However, long sonication process was known to open the tube end and fragment the tube length [4, 6, 12]. Thus an optimum time for CNT sonication is desirable to minimize the structural damage [13].

High shear mixing is one of the most preferable techniques in dispersing the CNT in matrix phase. Hammel *et al.* [14] extruded nanofibers without addition of modifiers in Polypropylene (PP) resin and compound for 5-30 minutes. The aggregate of fibers after the compounding process was found to be individually dispersed. As a result, they achieved improvement in Young Modulus of about 90% after reinforcing the fiber in PP. Li *et al.* [15] compounded 0.5 to 10 wt% of CNT in polyethylene (PET) and observed that the CNTs were homogeneously dispersed in PET matrix. As CNT concentration increased, the viscosity of the melt composite increased and led to stronger shearing thinning effect. However, by prolonging the extrusion process, the fiber tend to break down due to the shear process that destroyed the filler agglomeration and conductive network [16].

In this paper, the MWCNT/PDMS nanocomposite was compounded by using ultrasonic and twin screw extruder to understand the effects of the different processing techniques. The CNT sonication process was performed in liquid medium to break down the CNT aggregates and disperse them well in the suspension. Use of high shear twin screw mixer also tends to fragment the entangled CNT into short tube length. The tensile property was characterized by using Instron and the resulting micro-structure was observed under Scanning Electron Microscope (SEM).

2. Experimental

2.1. Materials

Polydimethylsiloxane (PDMS) type PP2-OE^{TM}41, which consists of two parts, was obtained from Gelest, Morrisville, PA and used as the matrix. Raw multi-walled CNT (Nanocyl 7000) with diameter of 9.5nm, length of 1.5μm and surface area of 250-300m^2/g was supplied by Nanocyl S. A. (Belgium). They are produced by CVD process and their purity is 90%. Toluene, which was supplied by Sigma Aldrich, was used as dispersing medium for the tubes when compound using ultrasonic method.

2.2. Preparation procedures

Ultrasonic and high shear twin screw extrusion were used to prepare the MWCNT/PDMS composites. Firstly, ultrasonic is one of the preferable methods. It delivers high levels of vibrational energy to the suspension. In this work, the as received MWCNT (>90% purity) was added into toluene using the

required volume fraction loading. The suspension was then sonicated using ultrasonic tip until the MWCNT was completely dispersed in the toluene solvent. PDMS part A was then added inside the MWCNT/toluene suspension and the sonication process was continued for another 40 minutes. Next, the MWCNT/PDMS/toluene mixture was stirred vigorously using mechanical stirrer at 70^0C so as to remove the toluene. In next step, part B that consists of the curing agent was added with continuous stirring. The uncured composite was then cast on the mould and placed under vacuum to remove the trapped air. After de-gassing, the solution was then pressed and cured to desired thickness by using compression molding at 55^0C for 4 hours.

Another preferable method is to use high shear mixer such as twin screw extruder. Solvent was not required when using the twin screw extruder. PDMS part A was injected inside the DSM Micro 15 mini extruder. The screw speed was set to 200 rpm and maintained for 2 minutes. Then the desired amount of carbon nanotubes were mixed together with PDMS part A. The mixture was mixed together for 10 minutes. After that, part B (curing agent) was injected into the extruder machine and the process was continued for another 5 minutes. After that, the uncured composite was extruded on the mould, followed by vacuum as to release the trapped air. The uncured composite was then pressed and cured with compression molding at 55^0C for 4 hours.

2.3. Characterization of sample

Tensile tests were conducted on Instron 5566, equipped with a video extensometer. The gauge length and cross-head speed used for the cured composite were 40mm and 50mm/min, respectively, at room temperature. The morphologies of fractured surface of the composite were observed with a scanning electron microscope (SEM) (JEOLJSM-6300F).

3. Results and discussion

Typical stress strain diagram are given in Figure 1 and Figure 2. For both processing systems, presence of MWCNT was shown to act as reinforcing filler that tend to increase the strength of the composites. A reinforcing effect was achieved by an efficient filler-matrix stress transfer, which can be obtained by a good adhesion between filler and matrix [17, 18]. The stress and strain level were found to increase at the same time by the addition of MWCNT. At a low strain modulus $\leq$5%, the result indicated the filler-filler networks in the composite. High filler loading with high surface area provided higher filler networking [19]. From this result, it is deduced that the reinforcing effect of MWCNT in the PDMS is obvious. As for ultrasonic processing composite, the strain of the composite was found to increase up to 1.5 vol% addition of filler loading. However, the strain slightly reduced when reaching 2.0 volume % of filler loading. A possible reason is at high filler concentration, the composite becomes stiffer due to large entanglement of CNT in the silicone resin. High shear mixer tends to break the CNT bundle into smaller size of aggregates or individual tubes in the silicone rubber. As can be seen from Figure 2, the strength of the MWCNT/PDMS increased proportionally with the filler content. High shear twin screw extruder is capable on breaking down high volume of CNT aggregates and disperses them well in the silicone rubber. Therefore, high energy is needed to separate a CNT bundle and reduce the tube entanglement [20].

Table 1 tabulates the mechanical properties for ultrasonic and mini extruder compounding process of the MWCNT/PDMS nanocomposites. The elongation at break at modulus 100 indicates that during stretching takes place, there is an interfacial slippage occurred between the tubes and silicone rubber matrix [21]. Strong bonding between filler and matrix needs higher strain to pull apart the filler from the matrix. A good filler dispersion exposed the tubes surface area to adhere with the silicone rubber and hence, prevent aggregation of the tubes. The property of elastomer is controlled by the degree of the cross-links in the network. The MWCNT in this work was used as received and therefore, there is no possible chemical reactions can occur between the tubes and the silicone rubber. Interactions may occur between the MWCNT and rubber molecules through entanglements and classical non-bonded interactions [3].

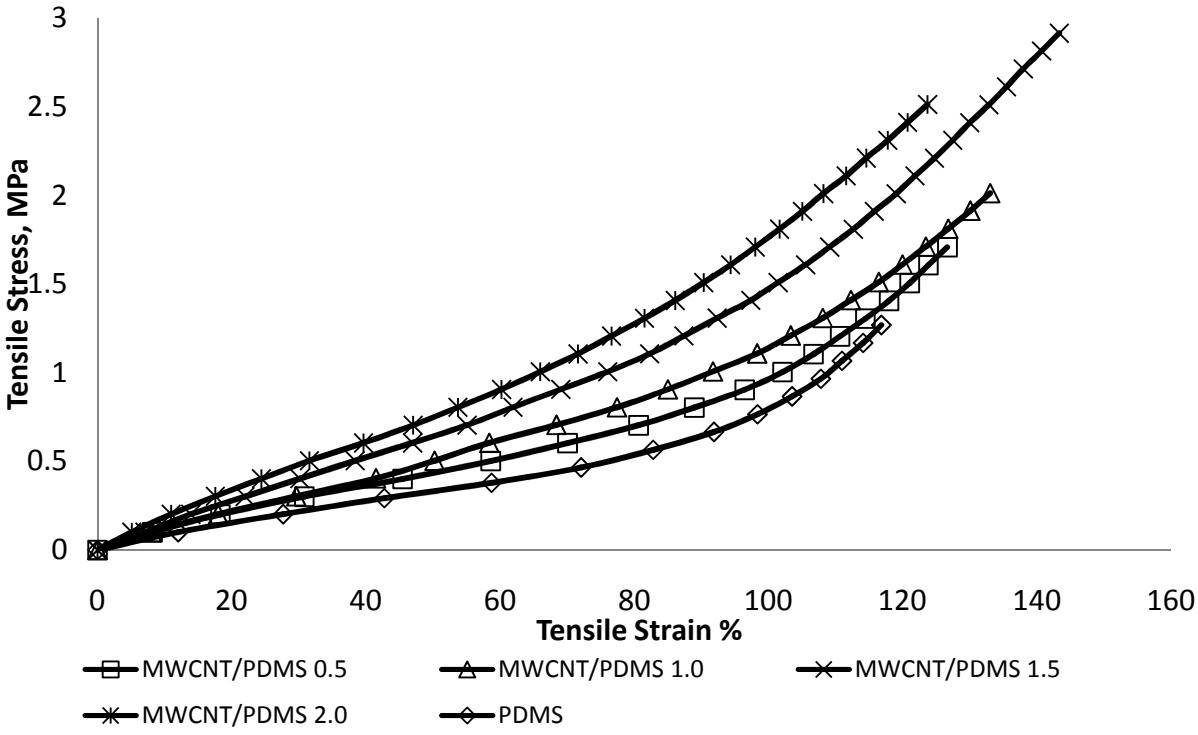


Figure 1. Typical stress-strain curves for MWCNT/PDMS nanocomposite by sonication process ranging from 0.5 to 2.0 vol% of filler content

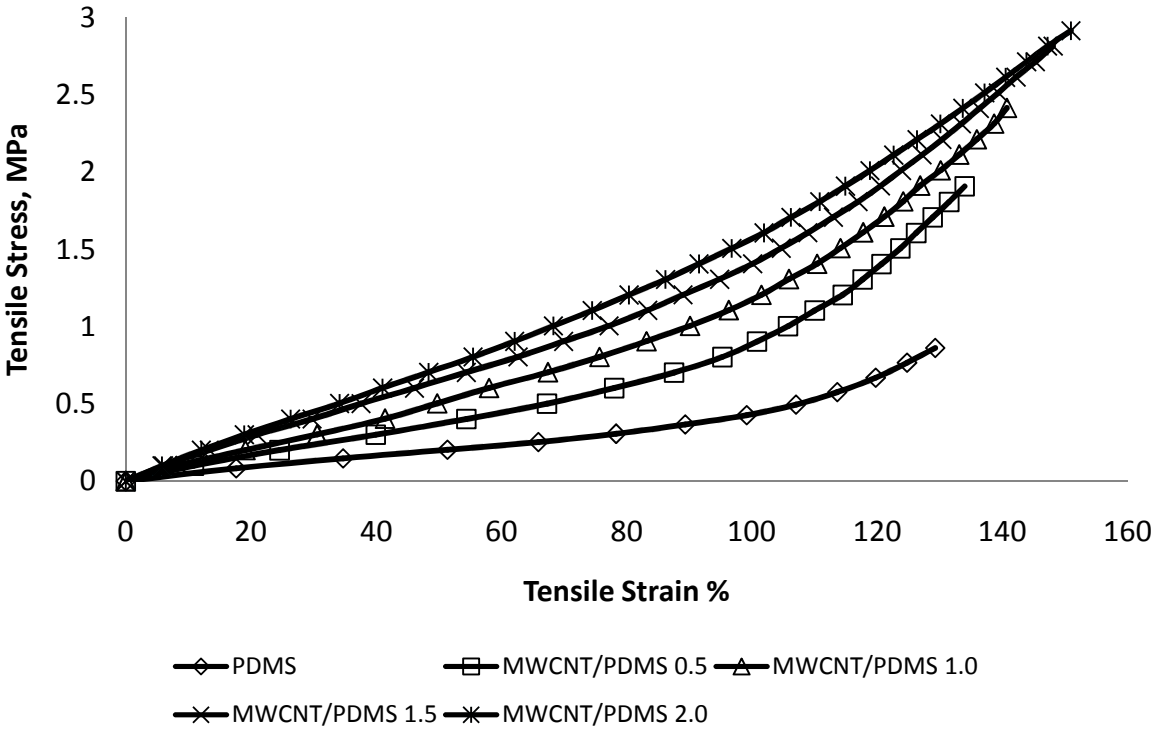
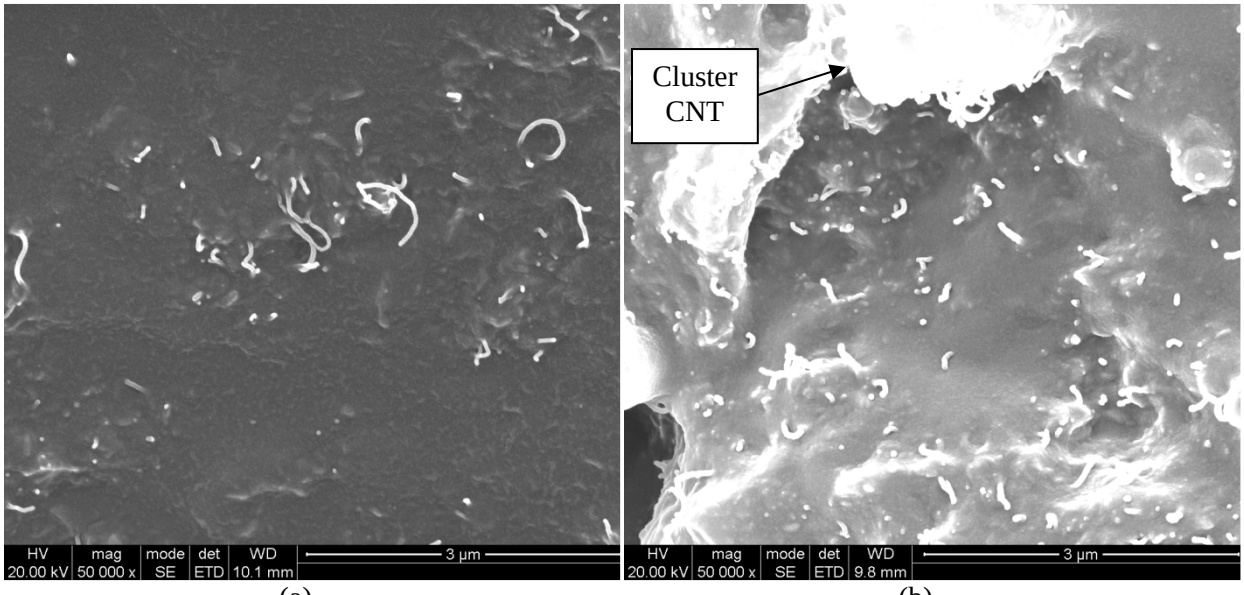


Figure 2. Typical stress-strain curves for MWCNT/PDMS nanocomposite by twin screw extruder process ranging from 0.5 to 2.0 vol% of filler content

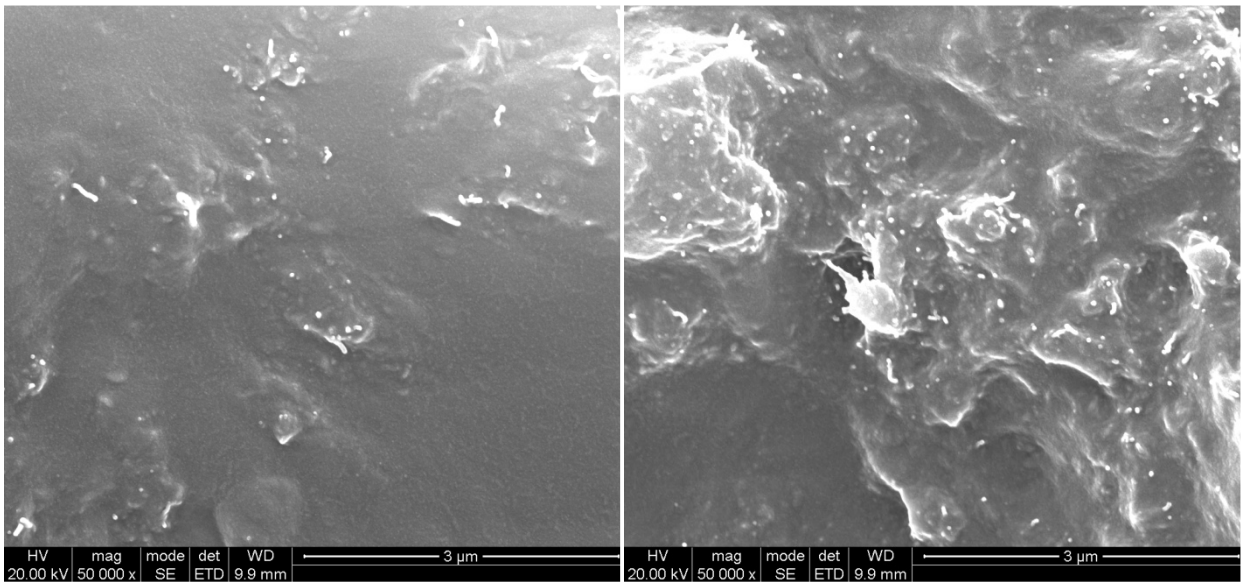
Table 1. The mechanical properties of the MWCNT/PDMS composites

Method	Nanocomposites	Modulus at 100% elongation (MPa)	Elongation at break (%)
	PDMS	0.6735 ± 0.03	129.67 ± 5.83
Ultrasonic	MWCNT/PDMS 0.5vol%	0.9557 ± 0.05	132.69 ± 2.51
	MWCNT/PDMS 1.0vol%	1.0048 ± 0.03	139.71 ± 4.61
	MWCNT/PDMS 1.5vol%	1.4785 ± 0.02	140.48 ± 3.81
	MWCNT/PDMS 2.0vol%	1.4061 ± 0.02	101.90 ± 12.38
Mini extruder	MWCNT/PDMS 0.5vol%	0.9461 ± 0.02	132.09 ± 5.29
	MWCNT/PDMS 1.0vol%	1.1805 ± 0.02	132.43 ± 3.25
	MWCNT/PDMS 1.5vol%	1.5265 ± 0.04	141.10 ± 2.72
	MWCNT/PDMS 2.0vol%	1.6081 ± 0.03	149.34 ± 3.85

The tensile fractured surfaces of the composites are presented in Figure 3. Figure 3a and Figure 3b indicate the fracture surface of MWCNT/PDMS compound by means of ultrasonic. As can be seen, the aggregate MWCNT is broken down at low filler content. The presence of a high amount of MWCNT seemed to make the dispersion in silicone rubber much difficult, which is as apparent in Figure 3d. As a consequence, the tensile strength slightly reduced due to the presence of cluster MWCNT. Compared with the SEM images in Figure 3c and Figure 3d, the MWCNT was found dispersed throughout the silicone rubber matrix. The obvious difference that can be observed from ultrasonic and twin screw extruder method is the tube length. High shear process induced shortening of tube length, which tends to reduce the surface area of the tubes. As a matter of fact, it increases the possibility to disperse the short tubes throughout the resin during compounding process.



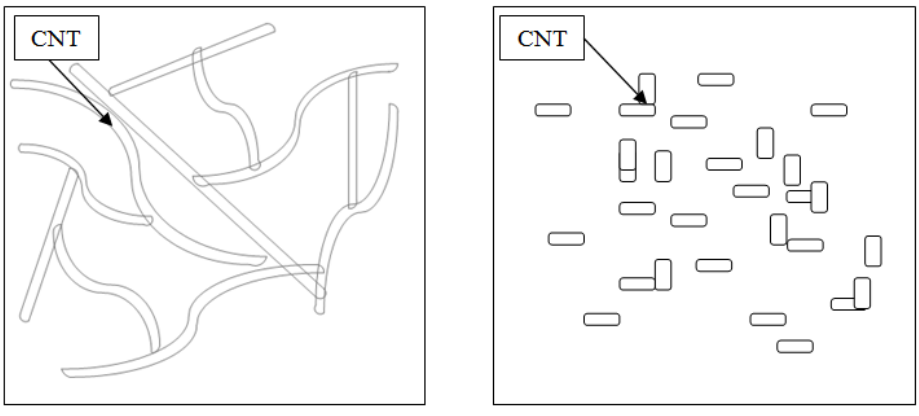
(a) (b)



(c) (d)

Figure 3. SEM micrograph of the fracture surface of: (a) 0.5 vol% MWCNT/PDMS nanocomposite compound by ultrasonic, (b) 2.0 vol% MWCNT/PDMS nanocomposite compound by ultrasonic, (c) 0.5 vol% MWCNT/PDMS nanocomposite compound by twin screw extruder, (d) 2.0 vol% MWCNT/PDMS nanocomposite compound by twin screw extruder

Figure 4 illustrates the schematic drawing on the behavior of the nanotubes in silicone rubber. The nanocomposites prepared by sonication method showed that the tubes intercalated within the silicone matrix (Figure 4a). Addition of toluene reduces the viscosity of the silicone resin and allows the silicone molecules to move freely through the galleries of nanotubes. The agglomerate tubes can expand and break down into small aggregates or single tubes as the silicone molecules pass through the entangle tubes. Therefore, this method tends to give better conductivity result as the tubes performed conductive network, which can be explained in the conductivity session. Compared to the extrusion method, the CNT degrades to a large extent. Twin screw extruder mixer is capable of cutting the tube length into short segments. Therefore, the tube was found to be dispersed very well in the silicone matrix. However, shortening the tube length can reduce the aspect ratio of the tubes due to the gradual breakage of CNT during high shear process. As a consequence, less interconnect tubes and less formation of conductive path (discussed in conductivity session).



(a) (b)

Figure 4. Schematic drawing of: (a) ultrasonic compound MWCNT/PDMS nanocomposite, (b) twin screw extruder compound MWCNT/PDMS nanocomposite

4. Conclusion

MWCNT/PDMS nanocomposites have been successfully prepared using ultrasonic and twin screw extruder methods. The dispersion of the tubes was examined by SEM, which indicates dispersion and random orientation of the tubes. Moreover, high shear extrusion process shortened the length of the tubes compared to ultrasonic process. The strength of the extrusion MWCNT/PDMS nanocomposites was found higher due to the good dispersibility of the tubes in the silicone matrix. However, excessive cutting of the tubes tend to reduce the thermal conductivity.

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